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# TECHNICAL NOTE

## D-194

CORRELATION FORMULAS AND TABLES OF DENSITY AND SOME  
TRANSPORT PROPERTIES OF EQUILIBRIUM DISSOCIATING  
AIR FOR USE IN SOLUTIONS OF THE  
BOUNDARY-LAYER EQUATIONS

By Nathaniel B. Cohen

Langley Research Center  
Langley Field, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
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CORRELATION FORMULAS AND TABLES OF DENSITY AND SOME  
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SUMMARY

Correlation formulas and tables of density, the product of density and viscosity, Prandtl number, Lewis number, and a diffusion function as functions of enthalpy and pressure are evolved from available property data. These functions are appropriate for calculating real-gas equilibrium boundary layers. The correlations cover a range in pressure from  $10^{-4}$  atmospheres to 10 atmospheres and an enthalpy range from 128.7 Btu/lb (corresponding to a temperature of  $540^{\circ}$  F) to 16,930 Btu/lb (corresponding to flight at approximately 29,000 feet per second).

INTRODUCTION

Consideration of air as a real gas in high-temperature flow phenomena requires knowledge of the thermodynamic and transport properties including the effects of dissociation and, at very high temperatures, ionization. Thermodynamic property data are presented in references 1 to 5 and tables and curves of transport properties are presented in references 1, 5, 6, and 7. In addition, reference 8 utilizes a simple binary model of "air atoms" and "air molecules" to develop approximate formulas for the properties, and reference 9 fits approximate analytic functions to the data of reference 5, such that all properties are functions of pressure and temperature.

With the exception of the Mollier chart of reference 3 and the charts of reference 4, all the aforementioned references present properties as functions of temperature with either pressure or density as a parameter. For boundary-layer investigations of air in chemical equilibrium, however, the enthalpy is the most convenient dependent variable for the energy equation, and the most desirable set of fluid properties would be one with enthalpy as the independent variable and pressure as the parameter.

Data in this form were used in references 10 and 11. During the course of equilibrium boundary-layer studies at the Gas Dynamics Branch of the Langley Research Center, certain correlation formulas and tables were evolved for the pertinent thermodynamic and transport properties of air in chemical equilibrium, and these are presented herein. They cover the range up to nearly complete dissociation but are not valid in the ionization region.

## SYMBOLS

$c$	mass concentration
$c_p$	constant-pressure specific heat
$c_{p,e}$	effective constant-pressure specific heat
$c_{p,f}$	frozen constant-pressure specific heat
$D_{ij}$	multicomponent diffusion coefficient
$\mathcal{D}_{ij}$	binary diffusion coefficient
$E$	internal energy per mol
$E^0$	energy per mol at zero absolute temperature
$e$	internal energy per mass, $E/m$
$e^0$	energy per mass at zero absolute temperature, $E^0/m$
$f(p,h)$	function defined by equations (23a) and (42)
$H$	local enthalpy per mol
$h$	local enthalpy per mass, $H/m$
$h_E$	reference enthalpy, $250\bar{R}T_{ref} = 2.119 \times 10^8 \text{ ft}^2/\text{sec}^2 = 8,465 \text{ Btu/lb}$
$k_f$	frozen conductivity
$k_e$	effective conductivity
$k_r$	reaction conductivity

m	molecular weight, mass per mol
$N_{Pr,f}$	frozen Prandtl number
$N_{Pr,e}$	effective Prandtl number
$N_{Le}$	Lewis number
n	molar density, mol per volume
p	pressure
$p_{ref}$	reference pressure, 1 atmosphere = 2,117 lb/sq ft abs
$\vec{q}$	heat-flux vector
R	gas constant per mass, $R_u/m$
$R_u$	universal gas constant per mol
T	temperature
$T_{ref}$	reference temperature, 273.16° K = 491.69° R
$\vec{V}_i$	average diffusion velocity of ith species
x	mol fraction
Z	compressibility, $p/\rho\bar{R}T$
$\mu$	viscosity
$\mu_{ref}$	reference viscosity, $3.584 \times 10^{-7}$ slugs/ft-sec
$\rho$	density, mass/volume
$\rho_{ref}$	reference density, $2.498 \times 10^{-3}$ slugs/cu ft

#### Subscripts:

1,2	evaluated at conditions $p_1, h_1$ and $p_2, h_2$ , respectively
A	atoms
E	evaluated at reference enthalpy $h_E$ and arbitrary pressure

i,j	property of ith and jth species, respectively
M	molecules
N	nitrogen atoms
N <sub>2</sub>	nitrogen molecules
O	oxygen atoms
O <sub>2</sub>	oxygen molecules

Barred quantities are for undissociated air.

### CORRELATION FORMULAS AND TABLES

In the correlations which follow, low-temperature thermodynamic and transport property data for air are taken from the NACA-NBS tables. (See ref. 1.) High-temperature thermodynamic properties are those of references 3 and 4, both of these being derived from the tables in reference 2.\* High-temperature transport properties are those of reference 5.

The correlations have been determined for the range

$$0.0152 \leq \frac{h}{h_E} \leq 2.0$$

$$10^{-4} \leq \frac{p}{p_{\text{ref}}} \leq 10$$

except where otherwise noted. The lower enthalpy limit corresponds to temperature of 540° R; the upper limit corresponds to the total enthalpy of the fluid encountered by a vehicle traveling in the atmosphere at a velocity of about 29,000 feet per second, a velocity somewhat larger than circular satellite velocity at the earth's surface. The pressure range should encompass those pressures encountered for all reasonable combinations of flight velocity and altitude up to an altitude of about 250,000 feet.

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\*References 3 and 4 use slightly different compositions and thus slightly different molecular weights for undissociated air. The difference is less than one-half of 1 percent and, in the light of the accuracy of the correlation formulas and tables found herein, is neglected. The present paper uses the constants for argon-free air of reference 3.

One other comment is appropriate at this point. The composition data of reference 4 indicate that, for all but the highest density levels, dissociation of oxygen is essentially complete before dissociation of nitrogen begins, and that the latter process is essentially complete before ionization of oxygen and nitrogen atoms begins. Thus, as discussed in reference 5, the value of the compressibility factor  $Z$  indicates approximately the reaction occurring at any given condition. For undissociated air composed of nitrogen and oxygen molecules in the ratio 4:1 by volume, the regions are  $1 < Z < 1.2$  for oxygen dissociation,  $1.2 < Z < 2.0$  for range of nitrogen dissociation, and  $2.0 < Z$  for the ionization of oxygen and nitrogen atoms. For the maximum enthalpy considered herein,  $h/h_E = 2.0$ , the values of  $Z$  for the six pressure levels were obtained from reference 4 and are tabulated below:

$p/p_{ref}$	Value of $Z$ for $h/h_E = 2.0$
$10^{-4}$	2.015
$10^{-3}$	2.003
$10^{-2}$	1.980
$10^{-1}$	1.954
$10^0$	1.912
10	1.857

These values indicate that, for all practical purposes, the present correlations remain within the range of nitrogen dissociation.

#### Density

Dimensionless plots of density ratio against enthalpy ratio at constant pressure for various pressure levels are shown in figure 1. The solid curve on the figure represents the function

$$\frac{\rho_E}{\rho} = 1 - 1.0477 \left[ 1 - \left( \frac{h}{h_E} \right)^{0.6123} \right] \quad (1)$$

The numerical coefficients in equation (1) were computed from the data at enthalpy ratios less than 1.6 by the method of least squares, and the function fits the data reasonably well over the range  $0.0152 \leq \frac{h}{h_E} \leq 2.0$

for all pressures shown. The maximum deviation in this range is about  $\pm 25$  percent at low enthalpy and the average deviation for all data is about  $\pm 6$  percent. Agreement is best in the range  $0.2 < \frac{h}{h_E} < 1.6$ .

The pressure dependence is established in figure 2 (density plotted against pressure at the reference enthalpy  $h_E$ ). The solid line is the function

$$\frac{\rho_E}{\rho_{ref}} = 0.0294 \left( \frac{p}{p_{ref}} \right)^{0.965} \quad (2)$$

computed by the method of least squares, and the difference between this function and the data points is negligible (less than one-half-percent deviation).

Equations (1) and (2) may be used to establish the arbitrary ratio  $\rho_1/\rho_2$  from the following identity:

$$\begin{aligned} \frac{\rho_1}{\rho_2} &\equiv \frac{\left( \frac{\rho_E}{\rho_2} \right)_{p=p_2} (\rho_E)_{p=p_1}}{\left( \frac{\rho_E}{\rho_1} \right)_{p=p_1} (\rho_E)_{p=p_2}} \\ &= \frac{1 - 1.0477 \left[ 1 - \left( \frac{h_2}{h_E} \right)^{0.6123} \right] \left( \frac{p_1}{p_2} \right)^{0.965}}{1 - 1.0477 \left[ 1 - \left( \frac{h_1}{h_E} \right)^{0.6123} \right] \left( \frac{p_1}{p_2} \right)^{0.965}} \quad (3) \end{aligned}$$

### Viscosity

The viscosity usually appears in boundary-layer work in the product of density and viscosity  $\rho\mu$ . A series of relations for  $\rho\mu$  as a function of  $p$  and  $h$  based on the data of reference 5 was given in reference 11. These different functions were used to fit different portions of the curves. A single function is derived in the present paper and is shown subsequently.

Plots of the ratio  $\rho_E\mu_E/\rho\mu$  against  $h/h_E$  at constant pressure in the range  $10^{-4} \leq \frac{p}{p_{ref}} \leq 10$  are shown in figure 3. The function

$$\frac{\rho_E\mu_E}{\rho\mu} = 1 - 1.0213 \left[ 1 - \left( \frac{h}{h_E} \right)^{0.3329} \right] \quad (4)$$

is plotted as the solid curve and was computed as a least-squares fit to the data for enthalpy ratios less than 1.6. Agreement between data and equation (4) is much better than was the case for density. Maximum deviation is about  $\pm 8$  percent and the average deviation in the entire range  $0.0152 \leq \frac{h}{h_E} \leq 2.0$  is about  $\pm 3$  percent.

The pressure dependence is shown in figure 4, where  $\frac{\rho_E^{\mu_E}}{\rho_{ref}^{\mu_{ref}}}$  is plotted against  $p/p_{ref}$ . The data and the curve, the latter a least-squares fit to the data and given by the function

$$\frac{\rho_E^{\mu_E}}{\rho_{ref}^{\mu_{ref}}} = 0.225 \left( \frac{p}{p_{ref}} \right)^{0.992} \quad (5)$$

agree within about one-half percent.

Equations (4) and (5) determine the arbitrary ratio  $\rho_1^{\mu_1}/\rho_2^{\mu_2}$  as follows:

$$\begin{aligned} \frac{\rho_1^{\mu_1}}{\rho_2^{\mu_2}} &\equiv \frac{\left( \frac{\rho_E^{\mu_E}}{\rho_2^{\mu_2}} \right)_{p=p_2}}{\left( \frac{\rho_E^{\mu_E}}{\rho_1^{\mu_1}} \right)_{p=p_1}} \frac{\left( \frac{\rho_E^{\mu_E}}{\rho_2^{\mu_2}} \right)_{p=p_1}}{\left( \frac{\rho_E^{\mu_E}}{\rho_1^{\mu_1}} \right)_{p=p_2}} \\ &= \frac{1 - 1.0213 \left[ 1 - \left( \frac{h_2}{h_E} \right)^{0.3329} \right]}{1 - 1.0213 \left[ 1 - \left( \frac{h_1}{h_E} \right)^{0.3329} \right]} \left( \frac{p_1}{p_2} \right)^{0.992} \end{aligned} \quad (6)$$

#### Heat-Transfer Parameters

The transport properties pertinent to the transfer of heat in a reacting gas mixture are the thermal conductivity and the diffusion coefficients. Correlations of these coefficients may be obtained in the same manner as was used for density and the density-viscosity product, but care must be taken in the definitions of the coefficients. The heat transfer can be treated in two ways; in the first, conduction

of heat by collisions of the atoms and molecules is kept separate from the heat transfer caused by the diffusion of the reacting gas species, and in the second (valid only for gas in chemical equilibrium), the two types of heat transfer are combined as an "effective conductivity." Both approaches and results are described in the following paragraphs.

Separate conduction and diffusion.— The heat-flux vector for a reacting mixture of perfect gases (neglecting pressure and thermal diffusion) is

$$\vec{q} = -k_F \text{ grad } T + \sum_i n_i H_i \vec{V}_i \quad (7)$$

where

$$\vec{V}_i = \frac{n^2}{n_i \rho} \sum_j m_j D_{ij} \text{ grad } x_j \quad (8)$$

In equations (7) and (8),  $k_F$  is the conductivity of the mixture due only to the collisions (the "frozen" conductivity),  $n_i$  and  $H_i$  are the molar density and specific enthalpy of the  $i$ th species, respectively,  $\vec{V}_i$  is the average diffusion velocity of the  $i$ th species relative to the mass averaged velocity of the mixture,  $D_{ij}$  is the multicomponent diffusion coefficient, and  $x_j$  is the molar concentration of species  $j$ ,  $n_j/n$ . The aforementioned relations are derived and discussed thoroughly in reference 12 (chs. 7, 8, and 11).

In general, the multicomponent diffusion coefficients are extremely difficult to express, and thus the energy flux by diffusion is difficult to evaluate. However, in the case of a binary mixture, these coefficients become the binary diffusion coefficients ( $D_{ij} = D_{ji}$ ) and the diffusion terms may then be evaluated. This approach is useful, therefore, in the case of dissociating air, which may be considered a binary mixture of "air atoms" and "air molecules" because of the similar molecular weights, thermodynamic properties and collision cross sections of oxygen and nitrogen. Such an approach was used in references 8 and 10. A parallel approach would not be useful for the ionization region, since at least three species, atoms, ions, and electrons exist.

For a binary mixture, then, the diffusional velocity is, from equation (8)

$$\vec{V}_i = \frac{n^2}{\rho} \frac{m_j}{n_i} D_{ij} \text{ grad } x_j \quad (9)$$

and the heat-flux vector is, from equations (9) and (7), by using the subscripts A and M for the two species, atoms and molecules,

$$\vec{q} = -k_f \text{ grad } T + \frac{n^2}{\rho} D_{AM} (H_{AM} \text{ grad } x_M + H_{MA} \text{ grad } x_A) \quad (10)$$

It is convenient to convert to a mass basis, in which

$$h_i = \frac{H_i}{m_i} = \frac{\text{Enthalpy/Mol}}{\text{Mass/Mol}} = \frac{\text{Enthalpy}}{\text{Mass}} \quad (11)$$

The mass concentration  $c_i$  is

$$c_i \equiv \frac{\rho_i}{\rho} = \frac{m_i n_i}{mn} = x_i \frac{m_i}{m} \quad (12)$$

where  $m$  is the mean molecular weight of the mixture given by either of the formulas

$$m = \sum_i x_i m_i \quad (13a)$$

$$\frac{1}{m} = \sum_i \frac{c_i}{m_i} \quad (13b)$$

Also, from the definitions of the concentrations,

$$\sum_i x_i = \sum_i c_i \equiv 1 \quad (14)$$

Equations (12) and (13) may be differentiated to yield

$$\text{grad } c_i = \frac{m_i}{m} \text{ grad } x_i - \frac{c_i}{m} \sum_i m_i \text{ grad } x_i \quad (15)$$

In the case of a binary mixture, from equations (13), (14), and (15),

$$\text{grad } c_A = -\text{grad } c_M = \frac{m_A m_M}{m^2} \text{grad } x_A = -\frac{m_A m_M}{m^2} \text{grad } x_M \quad (16)$$

When equations (11) and (16) are substituted into equation (10), the heat-flux vector becomes

$$\vec{q} = -k_F \text{grad } T - \rho_{AM} (h_A - h_M) \text{grad } c_A \quad (17)$$

The equations are now specialized for a constant-pressure process. This procedure is appropriate for the boundary layer because the only important components in the gradient are the partial derivatives in the direction normal to the surface, for which the pressure is constant. For a mixture in chemical equilibrium, since the mass concentrations are functions only of the state of the mixture

$$c_i = c_i(p, h) \quad (18a)$$

$$\text{grad } c_i = \left( \frac{\partial c_i}{\partial h} \right)_p \text{grad } h + \left( \frac{\partial c_i}{\partial p} \right)_h \text{grad } p \quad (18b)$$

Then the heat-flux vector is (for constant pressure)

$$-\vec{q} = k_F \text{grad } T + \rho_{AM} (h_A - h_M) \left( \frac{\partial c_A}{\partial h} \right)_p \text{grad } h \quad (19)$$

Because the enthalpy is the natural dependent variable for the equilibrium energy equation, the conduction term is rewritten in terms of enthalpy. From the definition for a mixture of perfect gases,

$$\left. \begin{aligned} h &\equiv \sum_i c_i h_i \\ h_i &= h_i(T) \end{aligned} \right\} \quad (20a)$$

and

$$\text{grad } h = \sum_i c_i \frac{dh_i}{dT} \text{ grad } T + \sum_i h_i \text{ grad } c_i \quad (20b)$$

and by using equation (18b) and the assumption of constant pressure

$$\text{grad } h = c_{p,f} \text{ grad } T + \sum_i h_i \left( \frac{\partial c_i}{\partial h} \right)_p \text{ grad } h \quad (21)$$

where the "frozen" specific heat is

$$c_{p,f} = \sum_i c_i c_{p_i}$$

and

$$c_{p_i} = \frac{dh_i}{dT}$$

Equation (21) is specialized for a binary mixture and solved for  $\text{grad } T$ . When the result is substituted into equation (19), there is obtained

$$-\vec{q} = \frac{\mu}{N_{Pr,f}} \text{ grad } h \left[ 1 + f(p,h) \right] \quad (22)$$

where

$$f(p,h) = (N_{Le} - 1) \left( \frac{h_A - h_M}{h_E} \right) \left( \frac{\partial c_A}{\partial \frac{h}{h_E}} \right)_p \quad (23a)$$

$$N_{Le} \equiv \frac{\rho_{AM} c_{p,f}}{k_f} \quad (23b)$$

$$N_{Pr,f} \equiv \frac{\mu c_{p,f}}{k_f} \quad (23c)$$

The three functions,  $f(p,h)$  (called herein the diffusion function),  $N_{Le}$  (Lewis number), and  $N_{Pr,f}$  (frozen Prandtl number), are purely properties of the equilibrium mixture and approximate data for the latter two are available for the dissociating region in reference 5. These are the "partial" coefficients in that reference. Correlations of these functions have been determined for equilibrium mixtures.

In figure 5 the "frozen" Prandtl number from reference 5 is plotted against enthalpy ratio for six pressure levels. The low-temperature data are that of reference 1. No simple analytic function was found to fit these data but, since the data approximately defined a unique curve for all pressures, a correlating table of Prandtl number was fitted. This function is given in table I and plotted in figure 5. The deviations in  $N_{Pr,f}$  are less than  $\pm 2$  percent. The deviations in the function  $1 - N_{Pr,f}$ , which appears in certain forms of the boundary-layer energy equation, are less than  $\pm 5$  percent. Thus, the function in table I is valid to these tolerances for the range  $0.005 \leq \frac{h}{h_E} \leq 2.0$ ,  $10^{-4} \leq \frac{p}{p_{ref}} \leq 10$ .

The diffusion function  $f(p,h)$  must be evaluated from the thermodynamic properties of the mixture as well as the Lewis number. The term  $\left(\frac{\partial c_A}{\partial h}\right)_p$  is evaluated as follows:

For air, the equation of state is

$$p = Z \bar{\rho} \bar{R} T = \rho R T \quad (24)$$

where  $\bar{R} = \frac{R_u}{\bar{m}}$  is the gas constant for undissociated air and  $R = \frac{R_u}{m}$  is the gas constant for the dissociating mixture. Then

$$Z = \frac{\bar{m}}{m} \quad (25)$$

The molecular weight of a mixture of gases is given by equation (13). Thus, for undissociated air

$$\frac{1}{\bar{m}} = \frac{\bar{c}_{O_2}}{m_{O_2}} + \frac{\bar{c}_{N_2}}{m_{N_2}} = \frac{\bar{c}_{O_2}}{32} + \frac{\bar{c}_{N_2}}{28} \quad (26)$$

From equations (13) and (25) for dissociating air,

$$\begin{aligned}
 Z &= \bar{m} \left( \frac{c_A}{m_A} + \frac{c_M}{m_M} \right) \\
 &= \bar{m} \left[ \left( \frac{c_O}{m_O} + \frac{c_N}{m_N} \right)_{\text{Atoms}} + \left( \frac{c_{O_2}}{m_{O_2}} + \frac{c_{N_2}}{m_{N_2}} \right)_{\text{Molecules}} \right] \quad (27)
 \end{aligned}$$

The mass concentrations of the four constituents may be found as functions of  $Z$  from equation (27) and an assumed composition of undissociated air. The undissociated air is assumed to be a mixture of oxygen and nitrogen molecules in the molar ratio of 1:4, which corresponds to a mass ratio of 0.222:0.778 ( $\bar{c}_{O_2} = 0.222$ ,  $\bar{c}_{N_2} = 0.778$ ). Then, regardless of the degree of dissociation,

$$c_O + c_{O_2} = 0.222 \quad (28a)$$

$$c_N + c_{N_2} = 0.778 \quad (28b)$$

Equations (27), (28), and (14) may be combined to yield the concentrations as functions of  $Z$  as follows:

For oxygen dissociation  $1.0 \leq Z \leq 1.2$ :

$$\left. \begin{aligned}
 c_A &= c_O = \frac{m_{O_2}}{\bar{m}}(Z - 1) \\
 c_N &= 0 \\
 c_{O_2} &= 0.222 - c_O \\
 c_{N_2} &= 0.778 \\
 \frac{\partial c_A}{\partial \frac{h}{h_E}} &= \frac{m_{O_2}}{\bar{m}} \frac{\partial Z}{\partial \frac{h}{h_E}}
 \end{aligned} \right\} \quad (29a)$$

For nitrogen dissociation  $1.2 \leq Z \leq 2.0$ :

$$\left. \begin{aligned} c_N &= \frac{m_{N_2}}{\bar{m}}(Z - 1.2) \\ c_O &= 0.222 \\ c_A &= c_O + c_N \\ c_{O_2} &= 0 \\ c_{N_2} &= 0.778 - c_N \\ \frac{\partial c_A}{\partial \frac{h}{h_E}} &= \frac{m_{N_2}}{\bar{m}} \frac{\partial Z}{\partial \frac{h}{h_E}} \end{aligned} \right\} \quad (29b)$$

Equations (29) depend upon the assumption, mentioned earlier, that dissociation of oxygen is complete before dissociation of nitrogen begins, and that the latter process is complete before ionization begins.

The term  $\frac{h_A - h_M}{h_E}$  in equation (23a) is an average enthalpy difference between the "air atoms" and "air molecules" and may be evaluated from the properties of oxygen and nitrogen atoms and molecules listed in reference 5. For the mixture

$$h = h_A c_A + h_M c_M \quad (30)$$

$$\left. \begin{aligned} h_A c_A &= h_O c_O + h_N c_N \\ h_M c_M &= h_{O_2} c_{O_2} + h_{N_2} c_{N_2} \end{aligned} \right\} \quad (31)$$

From equations (30) and (31)

$$\frac{h_A - h_M}{h_E} = \frac{c_O \frac{h_O}{h_E} + c_N \frac{h_N}{h_E}}{c_A} - \frac{c_{O_2} \frac{h_{O_2}}{h_E} + c_{N_2} \frac{h_{N_2}}{h_E}}{c_M} \quad (32)$$

The enthalpies of the constituents,  $h_O$ ,  $h_N$ ,  $h_{O_2}$ , and  $h_{N_2}$  may be evaluated from the tabulated internal energies in reference 5 and the relations

$$\frac{h_i}{R_1 T} = \frac{e_i}{R_1 T} + 1 = \frac{e_i - e_i^0}{R_1 T} + 1 + \frac{e_i^0}{R_1 T} = \frac{E_i - E_i^0}{R_u T} + 1 + \frac{E_i^0}{R_u T} \quad (i = O, N, O_2, N_2) \quad (33)$$

The term  $\frac{E_i^0}{R_u T} = \frac{e_i^0}{R_1 T}$  is a constant representing the internal energy of the gas at zero absolute temperature. It is herein taken as zero for the molecules and for the atoms is one-half the energy of dissociation per mol of the diatomic molecules. The dimensionless dissociation energies are, from reference 5

$$\frac{e_O^0}{R_O T} = \frac{E_O^0}{R_u T} = \frac{29,500^\circ \text{K}}{T}$$

$$\frac{e_N^0}{R_N T} = \frac{E_N^0}{R_u T} = \frac{56,600^\circ \text{K}}{T}$$

and,

$$\frac{e_{O_2}^0}{R_{O_2} T} = \frac{E_{O_2}^0}{R_u T} = \frac{e_{N_2}^0}{R_{N_2} T} = \frac{E_{N_2}^0}{R_u T} = 0$$

The internal energy relative to this constant  $\frac{E_i - E_i^0}{R_u T} = \frac{e_i - e_i^0}{R_1 T}$  is a function only of temperature and is given in table II(b) of reference 5.

Equation (33) may be rewritten, by using the definition  $h_E \equiv 250\bar{R}T$ , as

$$\frac{h_i}{h_E} = \frac{e_i^0}{h_E} + \frac{\bar{m}}{250m_i} \frac{T}{T_{\text{ref}}} \left( 1 + \frac{e_i - e_i^0}{R_1 T} \right) \quad (i = O, N, O_2, N_2) \quad (34)$$

where

$$m_O = 16$$

$$m_N = 14$$

$$m_{O_2} = 32$$

$$m_{N_2} = 28$$

and for the assumed composition, from equation (26),

$$\bar{m} = 28.8$$

The actual molecular weight of undissociated argon-free air is 28.86 (ref. 3), which compares very favorably with the assumed value shown above. The more correct value should be used in computing the gas constant  $\bar{R} = \frac{R_u}{\bar{m}}$ . The value 28.8 is used only in evaluating equations (29) and (34).

Values for the function  $f(p, h)$  (eq. (23a)) were computed for the six pressure levels and the enthalpy range  $0 \leq \frac{h}{h_E} < 2.0$ , by using equations (29), (32), (34), and the data of reference 5 for Lewis number and the enthalpies of the constituents. The values of  $\frac{\partial Z}{\partial \frac{h}{h_E}}$  in equations (29) were obtained from curves of  $Z$  against  $h/h_E$  plotted from the data of references 3 and 4. Note that below the level of oxygen dissociation where  $h/h_E$  is less than about 0.10,  $Z \equiv 1$ , and thus  $\frac{\partial Z}{\partial \frac{h}{h_E}} = f(p, h) = 0$ .

The results are shown in figure 6.

The spread with pressure level is moderately large and, strictly speaking, a correlating function should be a function of both enthalpy and pressure. However, it is felt that a function of enthalpy alone, representing the mean of the pressure spread, would be sufficiently accurate for boundary-layer purposes. (See Discussion.) Such a single function is given in table I and is shown in figure 6. The correlating function is assumed to be zero for  $\frac{h}{h_E} \leq 0.15$ , this value representing an average threshold of dissociation.

Although the viscosity, frozen Prandtl number, and diffusion function are sufficient to determine the coefficient of heat flow, the Lewis number itself is of interest.

The Lewis number data of reference 5 are shown in figure 7. No low enthalpy data are available but, since the Lewis number describes the diffusion processes, it has no application for equilibrium air at enthalpies below those required for dissociation. Dissociation is negligible below  $\frac{h}{h_E} = 0.1$  at the lowest pressure used herein; thus, lack of Lewis number data in this region is unimportant.

Figure 7 indicates that the Lewis number correlates roughly independent of pressure. A fitted set of data is given in table I and is shown as the solid curve in figure 7. The correlation function for  $N_{Le}$  is valid in the limits  $0.10 \leq \frac{h}{h_E} \leq 2.0$ ,  $10^{-4} \leq \frac{P}{P_{ref}} \leq 10$  within about  $\pm 10$  percent.

Although the correlations presented in this section are valid only for an equilibrium mixture, the general approach, ordinary conduction and diffusion effects being kept separate with a binary mixture, is also useful for nonequilibrium flows. In this more general case, equation (17) is appropriate, but the concentrations are functions of the reaction rates and the flow through the species continuity equations, and the coefficients are functions of concentrations as well as pressure and temperature. Few data are available for nonequilibrium processes, and they are not considered in the present report.

Lumping conduction and diffusion together.— The second method for evaluating the heat flux in a reacting mixture is closely related to the method just described. (They would be equivalent for a true binary mixture of reacting gases in equilibrium.) In this second method, the diffusion function is computed from the multicomponent diffusion coefficients, the specific reactions taking place being considered. The heat-transfer coefficient resulting from these diffusion processes is then considered a "reaction conductivity" and is added to the frozen conductivity. The method is restricted immediately to chemical equilibrium, but not to a binary mixture. The method is outlined and the results shown in the following.

For a multicomponent mixture of reacting gases, the heat flux is given by equations (7) and (8). If the gas is in chemical equilibrium, the molar concentrations are functions only of the state of the mixture, or

$$x_i = x_i(p, T) \quad (35a)$$

$$\text{grad } x_i = \left( \frac{\partial x_i}{\partial T} \right)_p \text{grad } T + \left( \frac{\partial x_i}{\partial p} \right)_T \text{grad } p \quad (35b)$$

The heat-flux vector is then, for a constant-pressure process,

$$-\vec{q} = (k_f + k_r) \text{grad } T \quad (36)$$

where the "reaction conductivity"  $k_r$  is defined

$$k_r \equiv - \frac{n^2}{\rho} \sum_i H_i \left[ \sum_j m_j D_{ij} \left( \frac{\partial x_j}{\partial T} \right)_p \right] \quad (37)$$

The quantity  $k_e \equiv k_f + k_r$  is considered an effective conductivity and includes ordinary conduction by collisions  $k_f$  and heat transfer by diffusion of reacting species  $k_r$ .

The mixture enthalpy is given by equation (20a) and is a property of the state of the mixture. Then,

$$\text{grad } h = \left( \frac{\partial h}{\partial T} \right)_p \text{grad } T + \left( \frac{\partial h}{\partial p} \right)_T \text{grad } p$$

and for a constant-pressure process

$$\text{grad } h = c_{p,e} \text{grad } T \quad (38)$$

where

$$c_{p,e} \equiv \left( \frac{\partial h}{\partial T} \right)_p = c_{p,f} + \sum_i h_i \left( \frac{\partial c_i}{\partial T} \right)_p \quad (39)$$

When the heat-flux vector is written in terms of the enthalpy gradient by using equation (38), there results

$$-\vec{q} = \frac{k_e}{c_{p,e}} \text{grad } h = \frac{\mu}{N_{Pr,e}} \text{grad } h \quad (40)$$

where the effective Prandtl number is defined as

$$N_{Pr,e} \equiv \frac{\mu c_{p,e}}{k_e} \quad (41)$$

The details of evaluating the reaction conductivity were shown in reference 13 where this method was first successfully applied. Hansen, in reference 5, applied the equations of reference 13 to the calculation of the effective Prandtl number in equilibrium air (the effective Prandtl number is Hansen's "Prandtl number"). His results are shown in figure 8 plotted against enthalpy ratio for the six pressure levels. There is some spread with pressure and it is caused mainly by the shift of the maxima and minima to slightly higher enthalpies at the higher pressures. Nevertheless, an approximate correlating function independent of pressure has been fitted to the data and is shown in figure 8 and in table II. Low-temperature data are not shown; at temperatures below the dissociation level ( $h/h_E$  is less than about 0.10), the frozen and effective Prandtl numbers are equal, and the data of reference 1 (correlated in table I) are appropriate.

Comparison of the two methods.— The two methods for expressing the transport coefficients of heat flux should, in principle, give identical results. They may be compared by equating equations (22) and (40), which gives another relation for computing the diffusion function

$$f(p,h) = \frac{N_{Pr,f}}{N_{Pr,e}} - 1 \quad (42)$$

The diffusion function given in equation (42) was computed from the data of reference 5 and the results are shown plotted against enthalpy ratio in figure 9. Again, the pressure spread is primarily caused by a shift in the two maxima and the minimum with pressure level. However, a single function has been fitted to the data and is shown as the solid curve on the figure. This function is listed in table II. In this case the correlating function has been set equal to zero for  $\frac{h}{h_E} \leq 0.13$ . For comparison, the correlating function which resulted from the data calculated from equation (23a) (the function of table I) is shown in figure 9 also, as the dashed curve. It is apparent that significant differences occur in the approximate range

$$0.3 < \frac{h}{h_E} < 1.2$$

The possible reasons for the differences in the two functions will be considered in the next section.

## DISCUSSION

The correlation formulas for density, and the density-viscosity product (eqs. (1) and (4), respectively) and the correlation tables for Prandtl number, Lewis number, and the diffusion function (tables I and II) give approximate variation of these quantities with enthalpy at constant pressure, independent of pressure level in the range  $10^{-4} \leq \frac{p}{p_{ref}} \leq 10$ .

In this form, these functions are particularly useful in integrating the boundary-layer equations because of the condition that the pressure is constant across the boundary layer. These correlations then represent the distribution of the respective functions across the boundary layer.

L  
6  
4  
5

From the boundary-layer point of view, the most important of these functions is the product  $\rho\mu$ , and figure 3 indicates that equation (4) represents the data very well. The question arises as to the accuracy of the viscosity data of reference 5, from which the present correlation has been derived. No direct experimental confirmation of the viscosity coefficient predictions of reference 5 exists. Some indirect experimental confirmation is apparent in the comparison of theoretical and experimental aerodynamic heat-transfer rates in reference 14, where the theory makes use of Hansen's viscosity coefficients. However, scatter in the data and the possibility of compensating errors in the viscosity coefficients or in the heat-transfer theory serve to deny complete confirmation of the calculated viscosities.

The transport properties computed in references 6 and 7 differ quantitatively somewhat from those of Hansen, the differences resulting from the differing assumptions made for the intermolecular potentials. Resolution of these differences must await more detailed description of the interaction potentials or direct experimental determination of the coefficients. In the present paper, reference 5 was used for transport properties because it gave data typical of the variety available, and because it covered the widest range in pressure and temperature.

The density correlation formula (eq. (3)) is not sufficiently accurate for the calculation of absolute density, but its value lies in obtaining solutions of the complete boundary-layer equations. The density ratio enters the boundary-layer equations explicitly only in the axial pressure gradient term in the momentum equation, and for high-temperature flows with cool walls, this term is not too important (ref. 15).

The frozen Prandtl number correlation fits the data very well, but this is not true of the diffusion function  $f(p,h)$  or the effective Prandtl number which includes the effects of diffusion. Nevertheless, the pressure-independent correlating functions should be useful for integrating the boundary-layer equations.

As was pointed out previously, the two approaches for computing the heat-flux coefficients for an equilibrium mixture of reacting gases led to the somewhat different results (see fig. 9). In principle, Hansen's calculations are somewhat more sophisticated in that his reaction effects are computed with mixtures of three constituents: oxygen atoms and molecules and nitrogen molecules in the oxygen dissociation region, and oxygen atoms and nitrogen atoms and molecules in the nitrogen dissociation region. In this way it is possible to consider that all atoms diffuse through all molecules but that the reactions involve only certain atoms and molecules. In the first method given herein, where a binary mixture of "air atoms" and "air molecules" was assumed, it is impossible to make this distinction. However, the manner in which these assumptions enter the resulting diffusion coefficients is not clear.

However, one of the assumptions used in both the present binary approach and in that of reference 5 appears to contribute to the discrepancy, that is, the assumption that oxygen and nitrogen dissociation regions do not overlap. This assumption does not have much effect upon the thermodynamic properties, and there is also probably little effect upon the viscosity and frozen conductivity, but a larger effect may be imposed upon the reaction conductivity and effective Prandtl number, which comes about as follows:

The assumption of separate oxygen and nitrogen regions leads to the requirement that  $\left(\frac{\partial Z}{\partial T}\right)_p$ , and hence  $\left(\frac{\partial Z}{\partial h}\right)_p$ , be zero at the transition between the two regions (at  $Z = 1.2$  for the assumed composition). However, the more correct thermodynamic data of references 2 to 4 show no such behavior. The slight overlap of dissociation regions therein keeps  $\left(\frac{\partial Z}{\partial h}\right)_p$  finite. Now the diffusion function, when separate conduction and diffusion are considered, is proportional to  $\left(\frac{\partial c_A}{\partial h}\right)_p$  (see eq. (23a)), which is in turn proportional to  $\left(\frac{\partial Z}{\partial h}\right)_p$  under the present assumptions.

The data computed from equation (23a) and plotted in figure 6 used values of this derivative obtained from the data of references 2 to 4 and thus the point at which  $Z = 1.2$  was not given by  $f(p, h)$  necessarily equal to zero. Had the thermodynamic data of reference 5 been used in conjunction with equation (23a) instead, where the condition of zero  $\left(\frac{\partial Z}{\partial h}\right)_p$  at  $Z = 1.2$  was enforced, the function  $f(p, h)$  would have necessarily been zero at this point. Such a calculation was carried out at one pressure level,  $p/p_{\text{ref}} = 10^{-4}$ , and the results are shown in figure 10. The solid curve represents equations (23a) using the thermodynamic property data of references 2 and 4. (This is the data of fig. 6 at this pressure.) The

dashed curve represents the data from equation (42) using the Prandtl number data of reference 5. (This is the data of fig. 9 at this pressure.) The third curve represents equation (23a) with the modification that Hansen's thermodynamic data (ref. 5) was used to compute  $\left(\frac{\partial Z}{\partial h}\right)_p$ , with the condition that

$$\left(\frac{\partial Z}{\partial h}\right)_p = 0$$

at

$$Z = 1.2$$

This condition imposes a minimum on the curve at  $\frac{h}{h_E} \approx 0.37$  with  $f(p, h)$  equal to zero. Under these conditions, the results of equation (23a) begin to take on the general appearance of the data from equation (42), the dashed curve, but with a much smaller second maximum.

On the other hand, Hansen has pointed out to the author in a private communication that the Butler and Brokaw formulas for thermal conductivity give maxima in  $k_e$  at slightly lower enthalpies than the maxima in  $c_{p,e}$  for each reaction. Since equation (42) may be expressed as

$$f(p, h) = \frac{k_e/k_f}{c_{p,e}/c_{p,f}} - 1$$

then the function of equation (42) should show a pronounced maximum followed by a distinct minimum for each reaction, a trend shown clearly in the data and correlating curve on figure 9 (from eq. (42)). If these trends are real, the assumption in the first method that the gas is a binary mixture of atoms and molecules may suppress the first minimum and second maximum, giving instead a flattened out curve in this region, exactly the behavior as shown in figure 6.

Real air should behave most nearly like a binary atom-molecule mixture where oxygen dissociation begins and where nitrogen dissociation nears completion. It is gratifying that the two methods do agree in these regions.

Fortunately, the question of choosing between the two diffusion functions for equilibrium flows is actually somewhat academic. Aside from the fact that many flow situations will not be in chemical equilibrium, even in the equilibrium cases, the diffusion effect is not

large in the dissociation region, and the differences resulting from using the different methods should be negligible. For example, for stagnation flow with fully dissociated air outside the boundary layer at a pressure of  $10^{-4}$  atmospheres and a constant Lewis number of 1.4, reference 10 predicts that the diffusion effect is to increase the heat transfer by a factor of about 15 percent over that for a Lewis number of unity ( $f(p,h) \equiv 0$ ). A correlation function for data computed from equation (23a) but using a constant Lewis number of 1.4 is shown in figure 6 and may be compared both to the function in figure 6 obtained by using the variable Lewis number of reference 5 and to the function in figure 9. Whereas, the  $N_{Le} = 1.4$  curve always has  $f(p,h) \geq 0$ , that is, it tends to increase the heat transfer toward the wall, the variable Lewis number curve and that of figure 9 are positive at low enthalpies and negative at higher enthalpies; this condition leads to the belief that in a boundary layer with high enthalpy at the outer edge and low enthalpy at the wall, the effect of diffusion will be self-compensating. One would then expect a total diffusion effect much smaller than that predicted by Fay and Riddell (ref. 10) with a negligible dependence upon which of the two diffusion functions was used. Quantitative comparisons and a more definite conclusion must await solutions of the boundary-layer equations using the pertinent real-gas properties.

#### CONCLUDING REMARKS

Correlation formulas and tables for density, the density-viscosity product, Prandtl number, Lewis number, and a diffusion function as functions of enthalpy and pressure have been developed from the available thermodynamic and transport property tables. Presented in this manner, the functions lend themselves to calculations of the equilibrium boundary layer in real-gas flow. The correlations cover a range in pressure from  $10^{-4}$  atmospheres to 10 atmospheres, and in enthalpy from 128.7 Btu/lb (corresponding approximately to a temperature of  $540^{\circ}$  R) to 16,930 Btu/lb (corresponding roughly to complete dissociation of nitrogen molecules, or to the total enthalpy of the air encountered by a vehicle in flight in the sensible atmosphere at a velocity of about 29,000 ft/sec).

Langley Research Center,  
National Aeronautics and Space Administration,  
Langley Field, Va., October 8, 1959.

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TABLE I.- CORRELATION TABLES FOR FROZEN PRANDTL NUMBER, LEWIS NUMBER,  
AND THE DIFFUSION FUNCTION OF EQUATION (23a)

Low temperature		High temperature			
$h/h_E$	$N_{Pr,f}$	$h/h_E$	$N_{Pr,f}$	$N_{Le}$	$f(p,h)$
0.005	0.770	0.10	0.768	1.355	*0
.010	.739	.20	.771	1.363	.190
.015	.708	.30	.755	1.268	.171
.020	.689	.40	.742	1.196	.087
.026	.680	.50	.731	1.154	.056
.031	.680	.60	.721	1.102	.039
.036	.684	.70	.712	1.045	.016
.042	.689	.80	.704	.986	-.016
.048	.696	.90	.698	.931	-.052
.053	.702	1.00	.693	.880	-.089
		1.10	.689	.832	-.124
		1.20	.686	.789	-.159
		1.30	.684	.750	-.191
		1.40	.683	.714	-.219
		1.50	.684	.684	-.244
		1.60	.686	.660	-.265
		1.70	.690	.637	-.267
		1.80	.695	.619	-.259
		1.90	.700	.604	-.235
		2.00	.707	.590	-.204

\*For  $\frac{h}{h_E} \leq 0.15$ ,  $f(p,h) = 0$ .

TABLE II.- CORRELATION TABLES FOR EFFECTIVE PRANDTL NUMBER AND THE  
DIFFUSION FUNCTION OF EQUATION (42)

$h/h_E$	$f(p,h)$	$N_{Pr,e}$
0.10	*0	0.740
.20	.231	.619
.30	.112	.688
.40	-.006	.758
.50	.210	.615
.60	.230	.593
.70	.198	.593
.80	.139	.608
.90	.075	.635
1.0	.016	.670
1.1	-.040	.711
1.2	-.092	.759
1.3	-.139	.806
1.4	-.181	.850
1.5	-.218	.888
1.6	-.250	.922
1.7	-.270	.949
1.8	-.279	.958
1.9	-.268	.947
2.0	-.235	.904

\*For  $\frac{h}{h_E} \leq 0.13$ ,  $f(p,h) = 0$ .

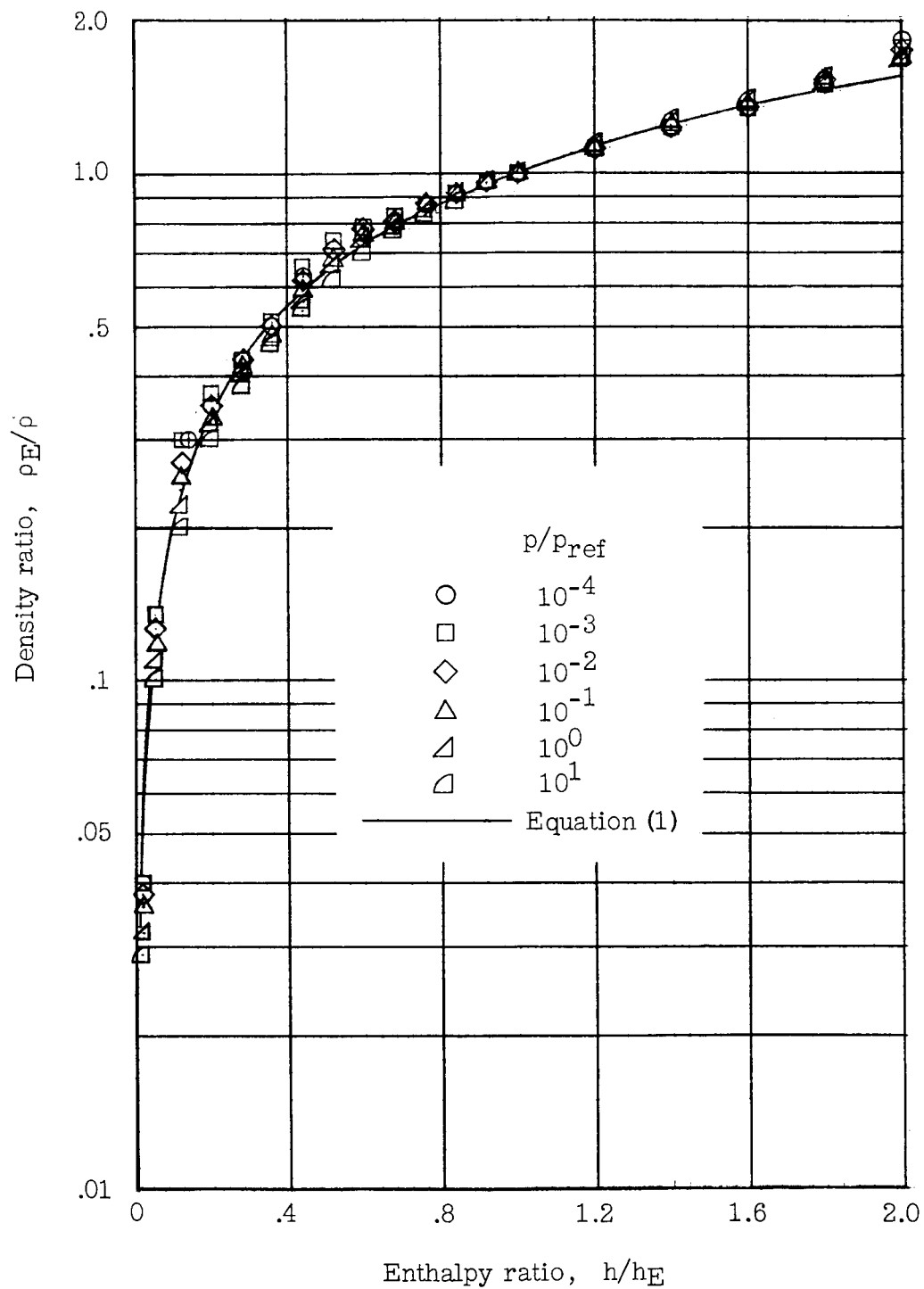


Figure 1.- Density ratio as a function of enthalpy ratio at various pressure levels.

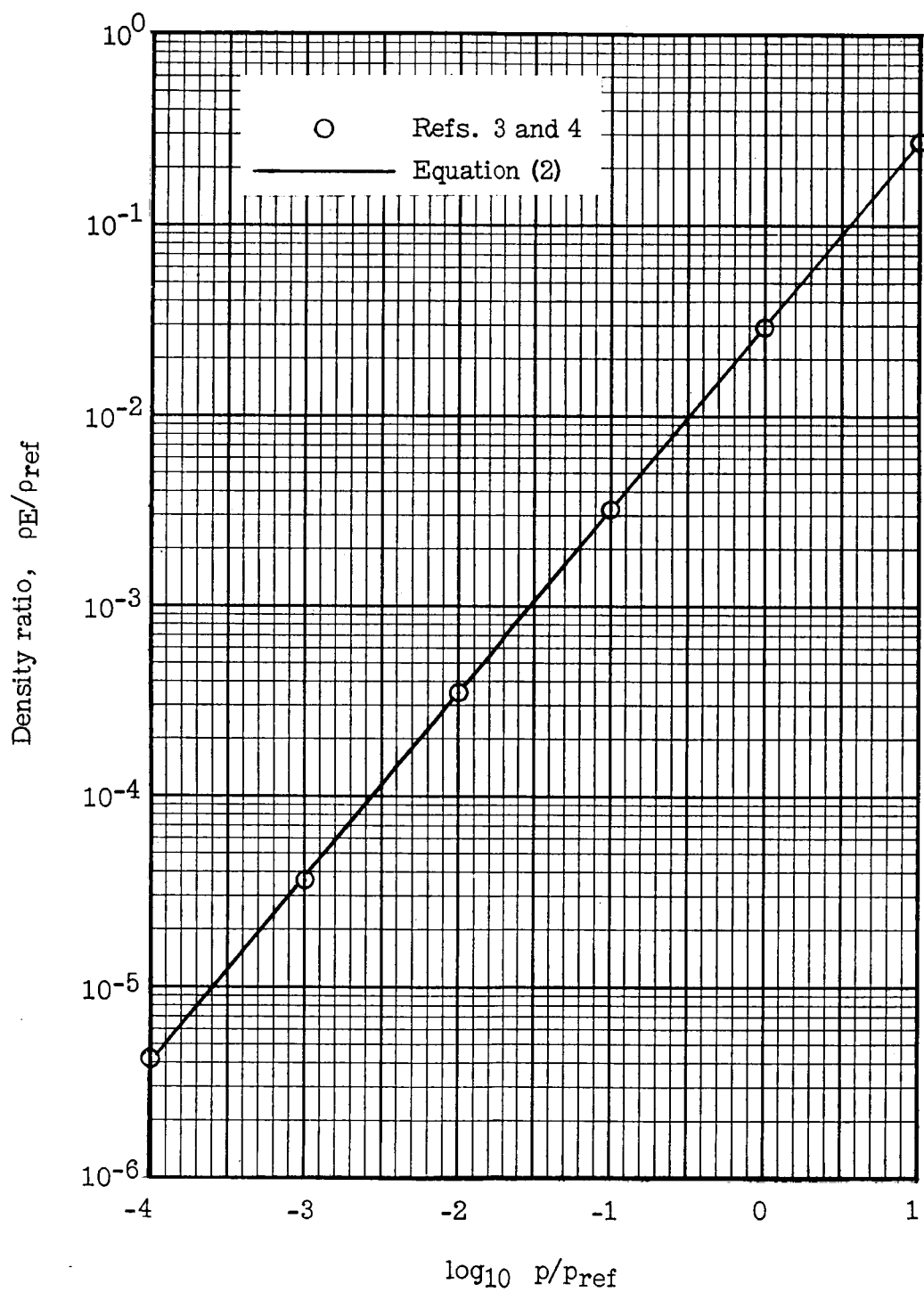


Figure 2.- Density as a function of pressure at the reference enthalpy  $h_E$ .

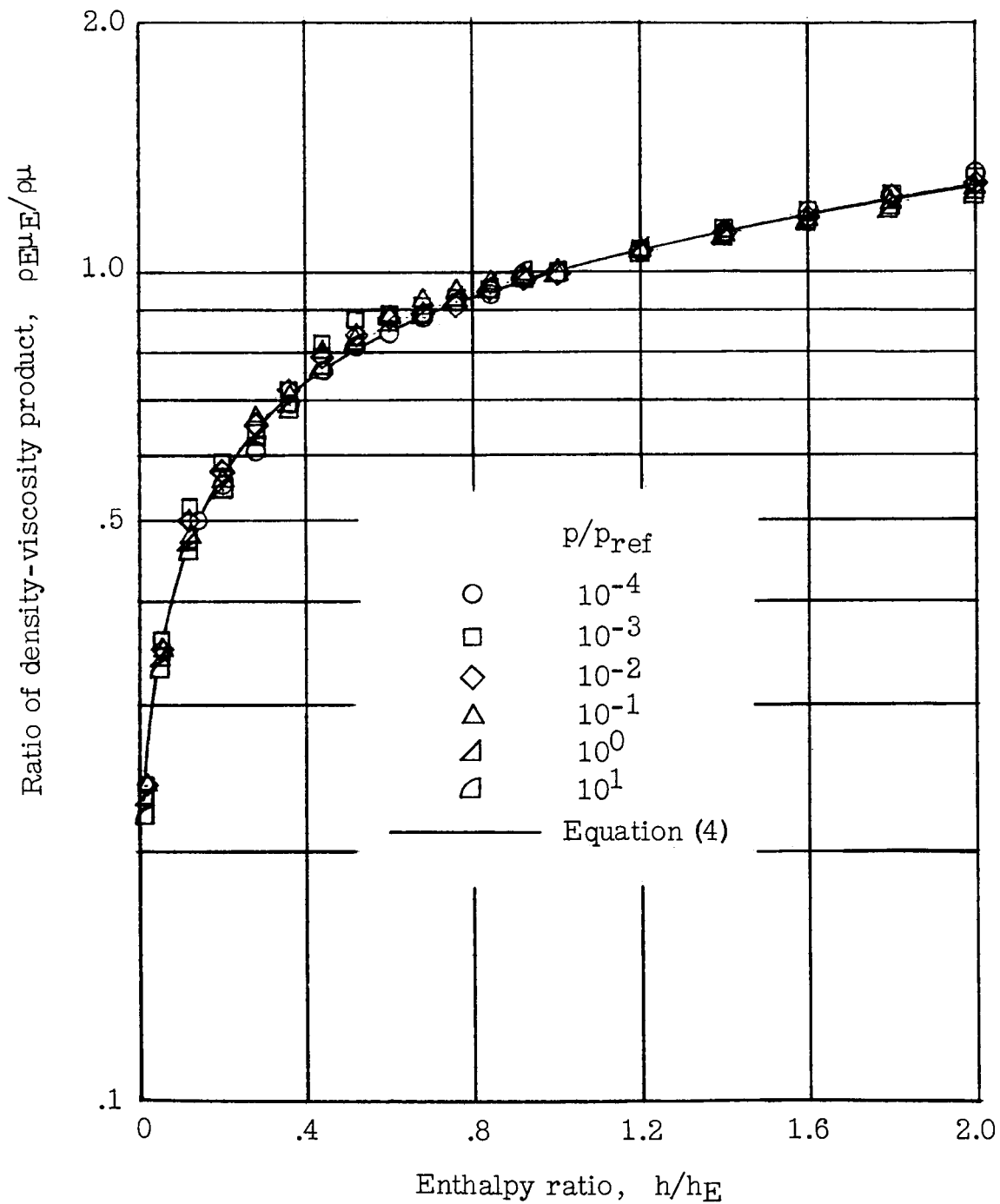


Figure 3.- Ratio of density-viscosity product as a function of enthalpy ratio at various pressure levels.

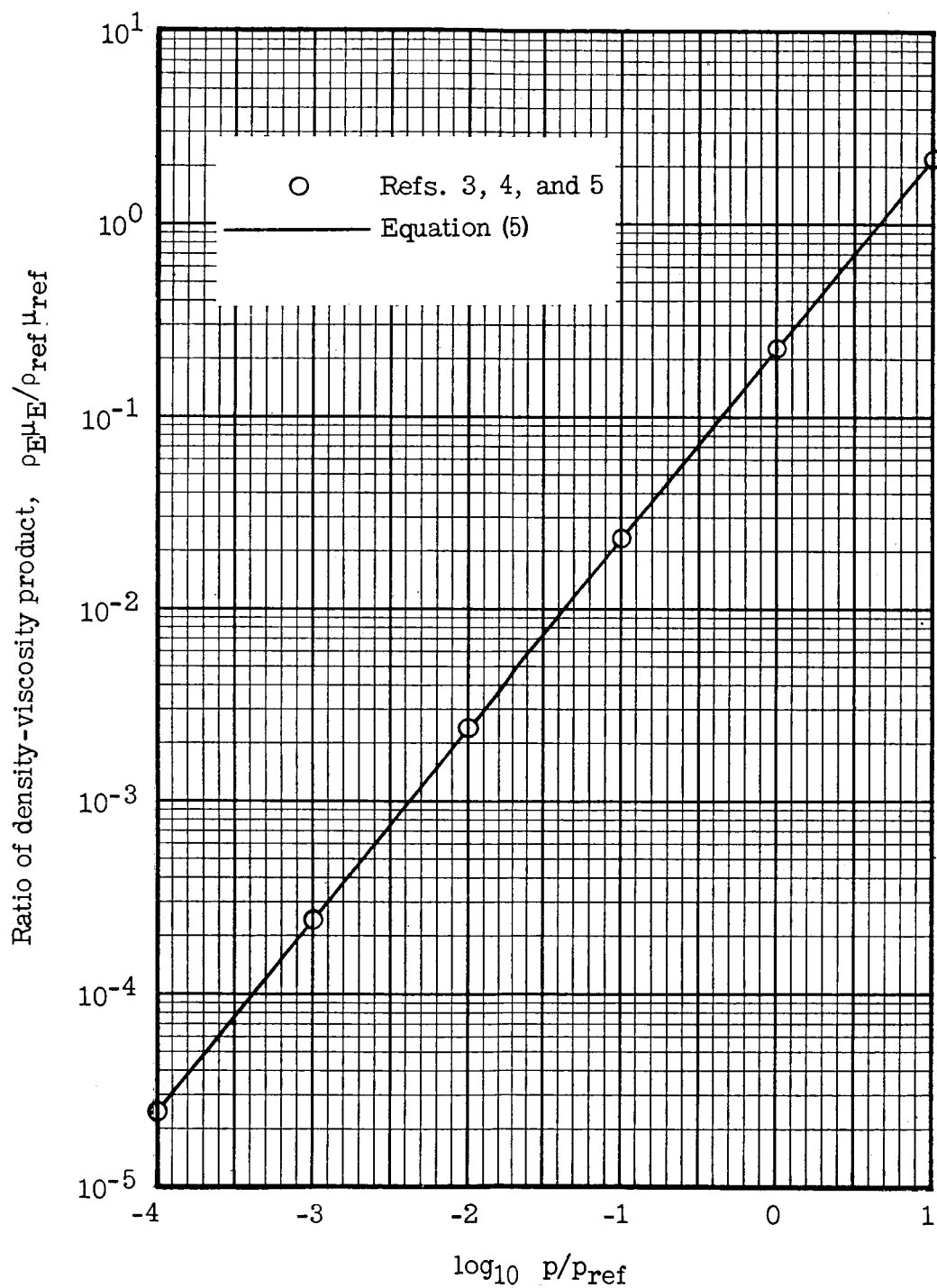


Figure 4.- Ratio of the density-viscosity product as a function of pressure ratio at the reference enthalpy  $h_E$ .

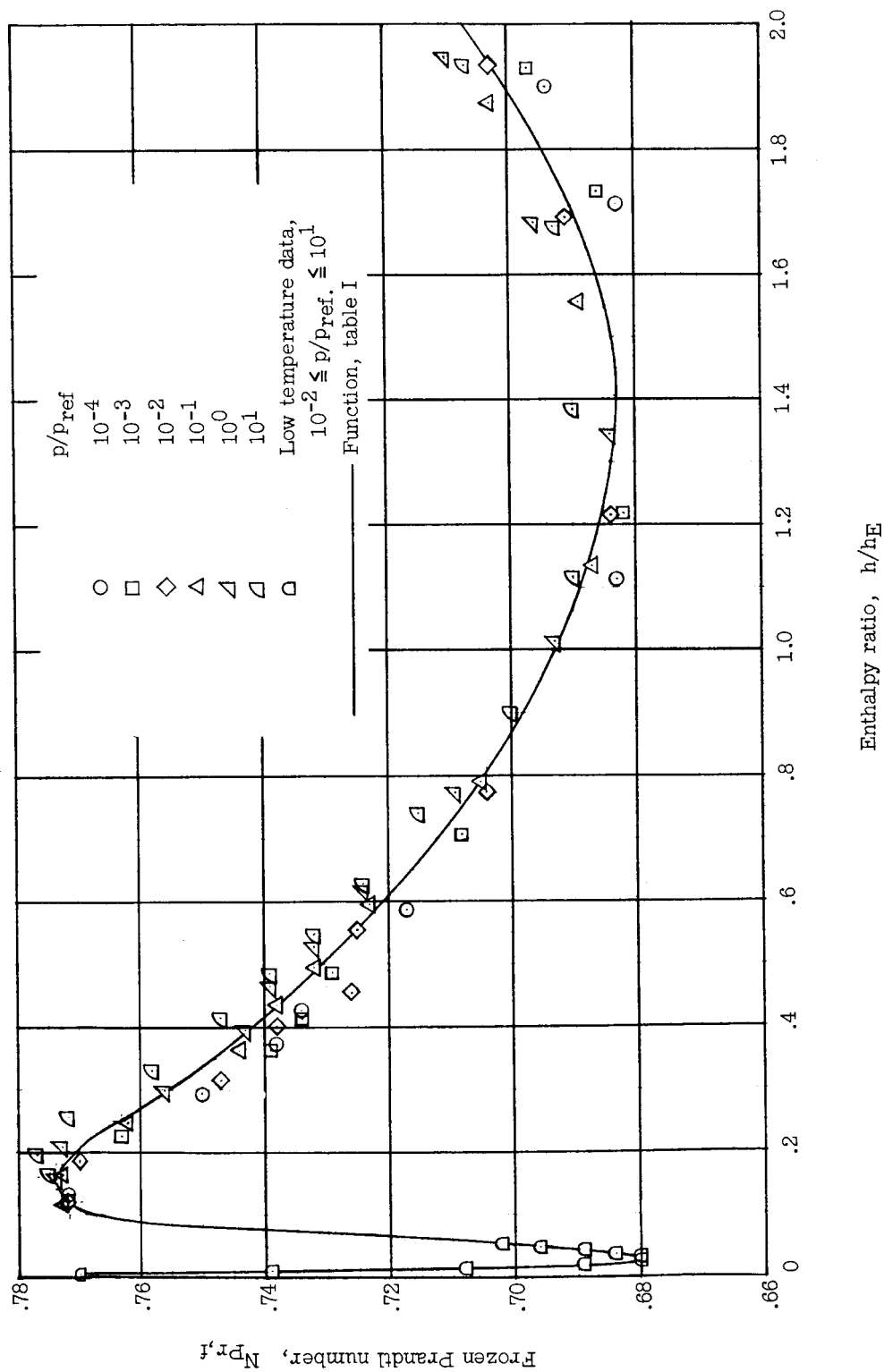


Figure 5.- Frozen Prandtl number as a function of enthalpy ratio at various pressure levels.

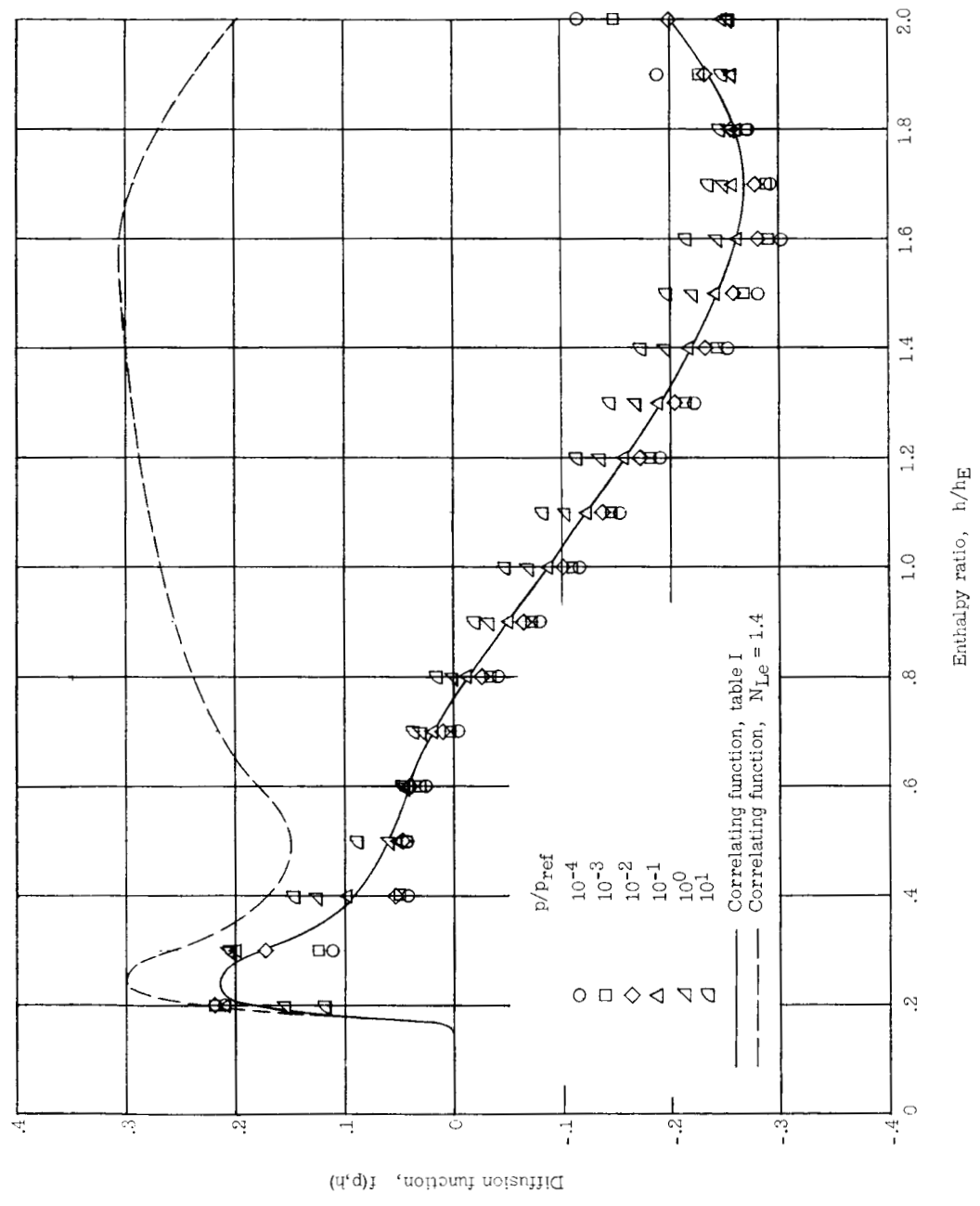


Figure 6.- Variation of diffusion function  $f(p,h)$  of equation (23a) with enthalpy ratio at various pressure levels.

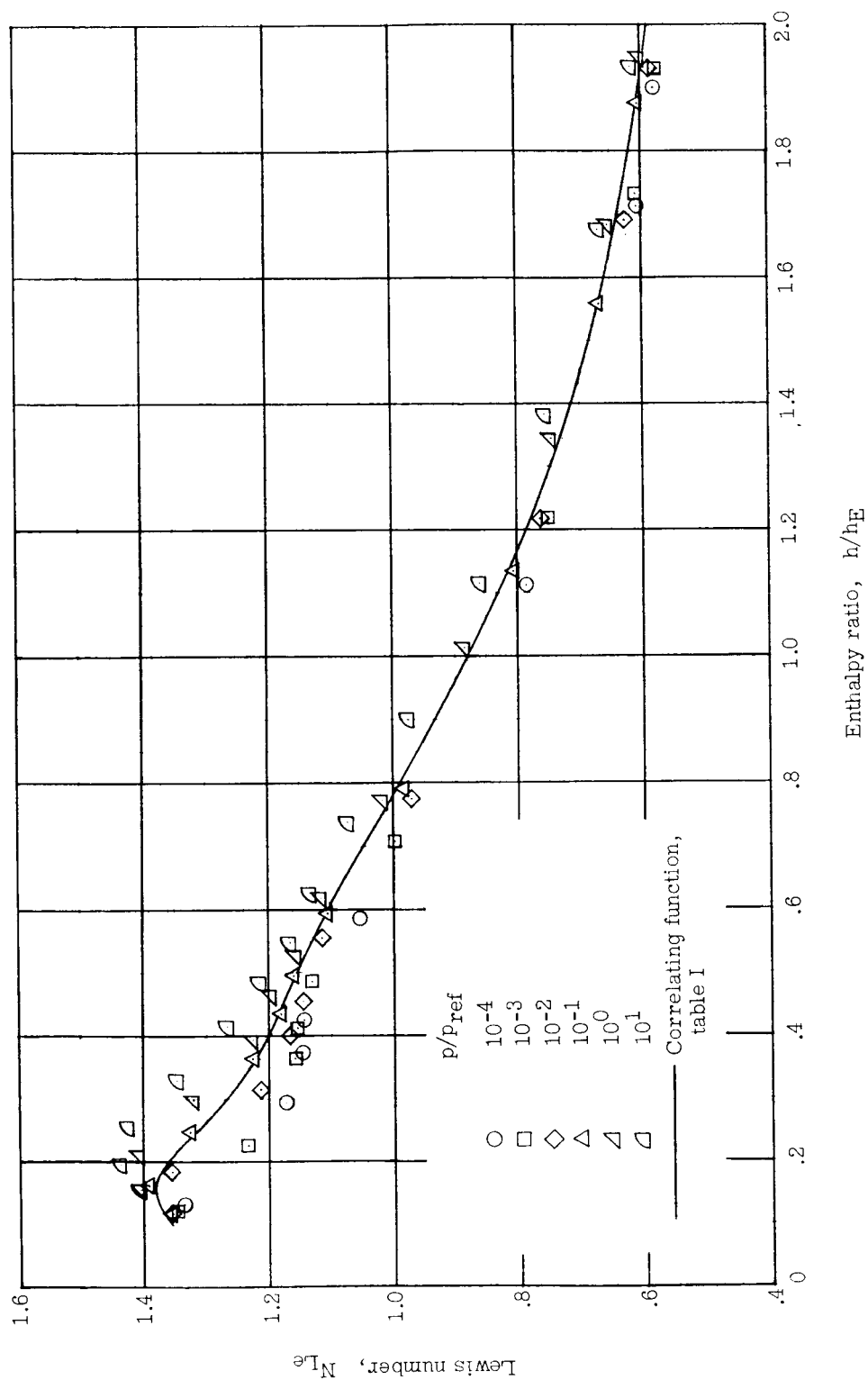


Figure 7.- Lewis number as a function of enthalpy ratio at various pressure levels.

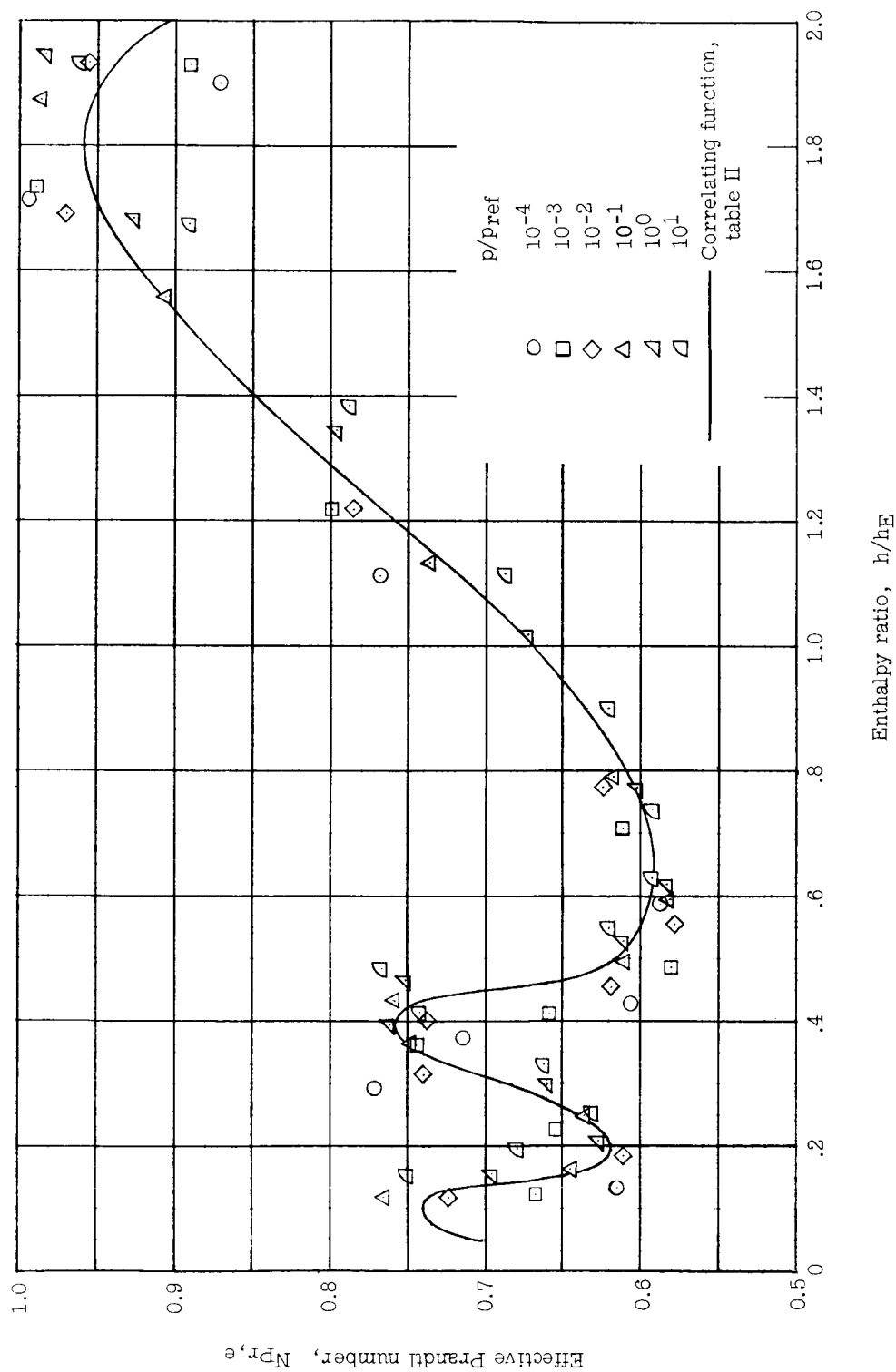


Figure 8.- Variation of effective Prandtl number with enthalpy ratio at various pressure levels.

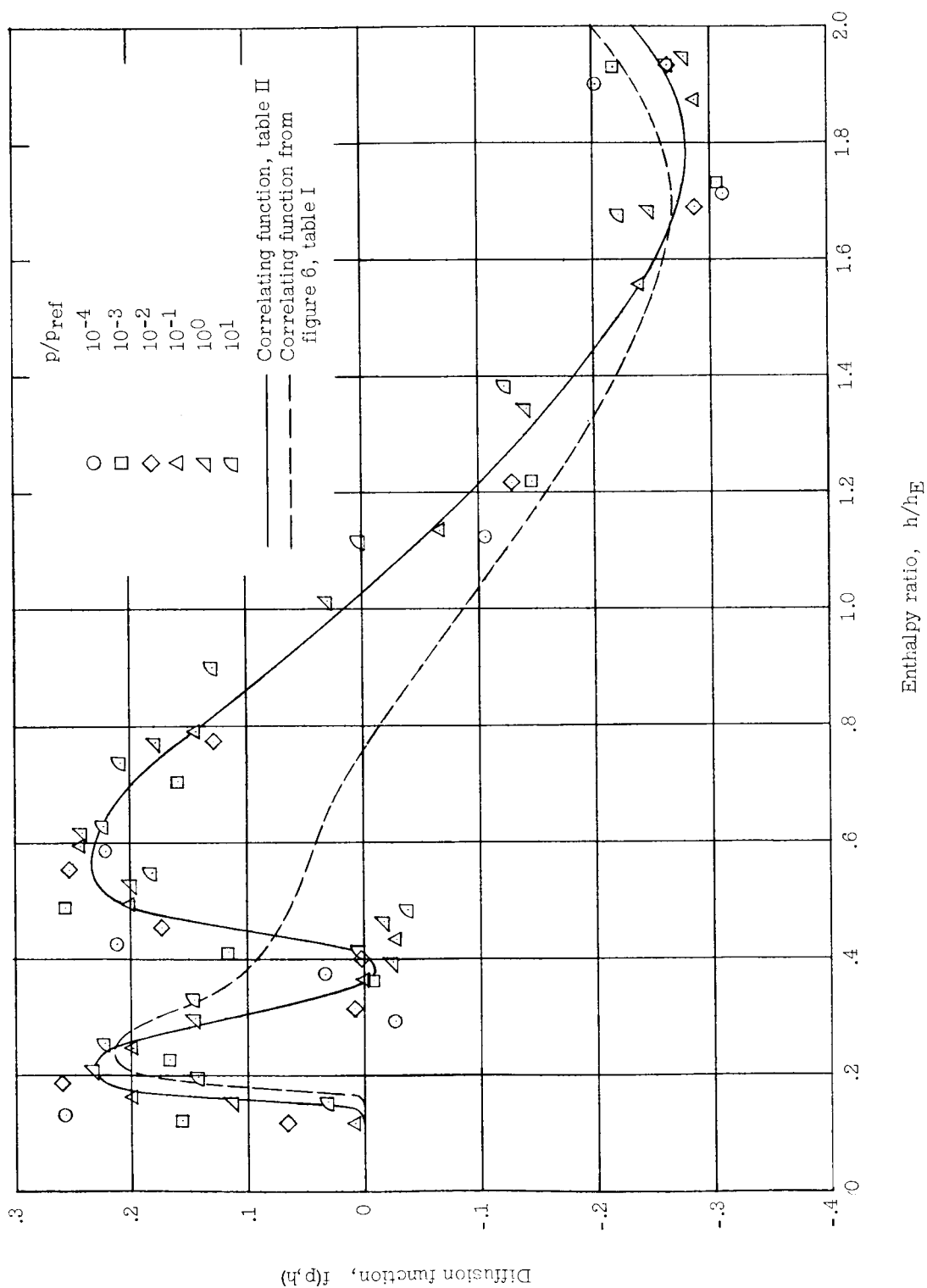


Figure 9.- Variation of diffusion function calculated from equation (42) and reference 5 with enthalpy ratio at various pressure levels.

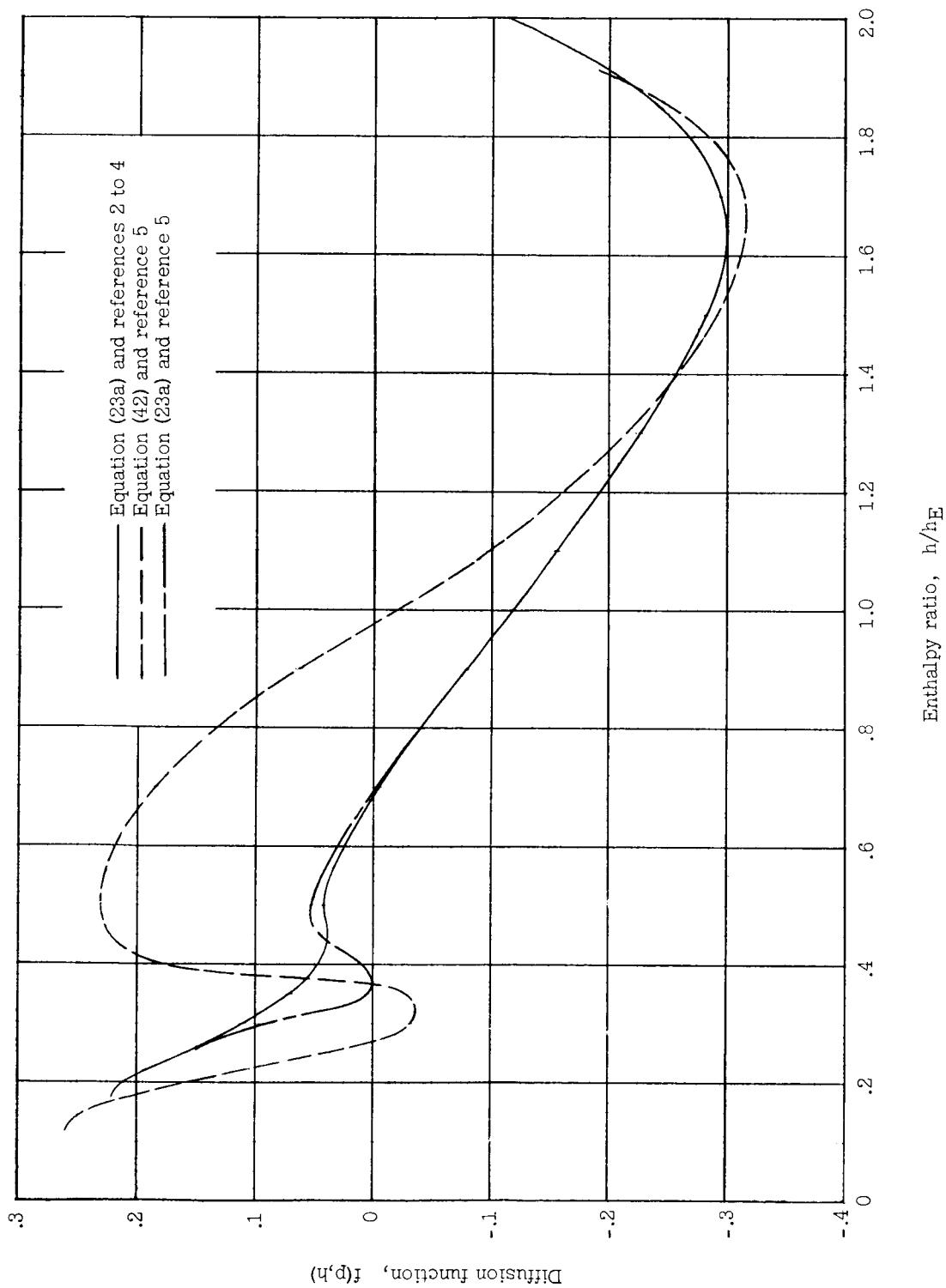


Figure 10.- Comparison of diffusion functions for a pressure level of  $10^{-4}$  atmospheres.